

B. EFFECTS OF ORGANICS ON ACTINIDES

Introduction

Naturally occurring organic compounds generated during the transformation of plant and animal debris over time and as a result of the synthetic activities of microorganisms are ubiquitous in surface and subsurface environments. For example, pore water from a well-developed soil environment usually contains dissolved organic carbon in quantities greater than 20 mg/l in top soils and in quantities of about 5 mg/l in subsoils. Dissolved organic carbon concentrations in groundwaters typically depend on the environment and are usually below 2 mg/l (Drever 1988). The decrease in concentrations of organic materials with increasing depth is attributed to chemical and biological degradation as well as to sorption on mineral surfaces. Sorption of organic materials onto mineral surfaces is considered the dominant contributing factor to the removal of organics from solution during percolation through the subsurface.

The interaction between organic materials and mineral surfaces in the natural environment is important to mineral surface geochemistry. Sorption of organic material onto mineral surfaces affects not only the solubility and charge of the organic materials in solution but also the properties of the mineral surfaces, such as their charge and hydrophobicity, thereby altering the reactivity of the mineral toward metal ions. A clear understanding of the effects of the organic materials that frequently coat mineral surfaces in natural environments will lead to improvements in the sorption models used to predict the mobility of radionuclides in natural aquatic environments (Choppin 1992).

The objective of this section is to summarize the laboratory results for the effect of organic materials on the sorption of plutonium and neptunium on selected mineral oxides and tuff material.

Experimental Procedures

Preparation of tuff and oxide minerals

Three synthetic iron oxides (goethite, hematite, and ferrihydrite), one synthetic aluminum oxide (boehmite), and a natural crushed-tuff material from Yucca Mountain (USW G4-270, a devitrified tuff) served as model sorbents. Methods for preparing the oxides are described in the literature (Kung and McBride 1989a, 1989b, 1991).

In brief, iron oxide was synthesized by reacting ferric chloride with dilute sodium hydroxide under slightly acidic conditions and was then aged at raised temperature for several days. X-ray powder diffraction (XRD) analysis confirmed the oxide to be pure goethite. The surface area of the goethite, calculated from nitrogen adsorption by the three-point BET method, was about 89.5 m²/g.

The ferrihydrite preparation involved the overnight hydrolysis of ferric salt at low pH followed by raising the pH with dilute sodium hydroxide and, finally, aging the mixture for two weeks at raised temperature. The surface area of the freeze-dried material was 91.5 m²/g. XRD analysis indicated a poorly crystalline product containing ferrihydrite.

Hematite was prepared by aging ferric nitrate solution at raised temperature for 3 days. The surface area of the freeze-dried material was 39.4 m²/g. XRD analysis confirmed that this material was well-crystallized hematite.

Boehmite was prepared by fast hydrolysis of aqueous aluminum chloride with sodium hydroxide, followed by mixing and aging. The surface area of the freeze-dried material was 324 m²/g. XRD analysis confirmed that this aluminum oxide was poorly crystallized boehmite, an aluminum oxyhydroxide.

The metal oxides were stored either in a freeze-dried state or in suspensions containing 0.1 M KCl. For those in suspensions, the solid concentration of these oxide suspensions was less than 20 mg/ml.

XRD analysis of the crushed-tuff material (USW G4-270, a devitrified tuff), obtained from S. Chipera, indicated that it was about 30% silica and 69% feldspar, the remainder consisting of trace amounts of layer silicates and iron oxide. Part of the tuff material was treated with a 15% hydrogen peroxide solution to remove any natural organic material from the tuff surface.

Preparation of organics and radionuclides

Catechol, alanine, DOPA, and NAFA were used as model organic materials. Catechol is a phenolic compound that may chelate with metal ions and undergo redox reaction with the metal. Alanine is an amino acid that will complex with the hard-acid type of metal ions in solution. DOPA, a naturally occurring amino acid commonly found in plant seedlings, pods, and broad beans, was chosen because it contains well-defined organic functional groups such as carboxylic acid, amine, and phenols. The catechol, alanine, and DOPA, purchased from Fluka Chemical Company with purity greater than 99%, were used as received. The NAFA, obtained from the International Humic Substances Society (IHSS), is identified by IHSS as a reference fulvic acid with the code number 1R105F and is prepared and homogenized from a designated aquatic source by IHSS.

Neptunium-237 was obtained from Amersham International (product code NGZ-44). The plutonium-239 stock solution was prepared in the Pu(V) oxidation state (this concentrated stock solution was obtained from P. Parmer at Los Alamos). The desired concentrations of neptunium and plutonium were diluted and stored in 0.1 M KCl solutions. Under the experimental conditions used in this work, the plutonium and neptunium are expected to exist as the chemical species PuO_2^+ and NpO_2^+ , respectively.

Sorption Measurements

DOPA sorption

Sorption isotherms were obtained by mixing the desired sorbent suspension and sorbate in Teflon or

polycarbonate centrifuge tubes. The initial DOPA concentrations ranged from 20 to 100 μM . The pH was adjusted by adding 0.05 M NaOH or HCl immediately after mixing. The tubes were capped and shaken for at least 20 hours at $22 \pm 1^\circ\text{C}$. The solid phase was separated from suspension by centrifugation. The supernatant was analyzed for unsorbed DOPA by ultraviolet spectrometry (Hewlett-Packard 8450A), and the amount of sorption was calculated by determining the difference between the initial and final concentrations. Potassium chloride was used as a background electrolyte to maintain an essentially constant ionic strength of 0.1 M.

Radionuclides sorption

A similar method was used to obtain plutonium and neptunium sorption isotherms. The amount of radionuclide in solution was determined by liquid scintillation counting (Packard 2550-TR/AB). The metal ions were introduced into the tubes after the pH in each suspension was adjusted. For the multisorbate systems, the organic sorbate was added before the radionuclide sorbate. Solution pH was measured after shaking. The carbon dioxide was not controlled in all the systems studied. For the initial sorption isotherms, about 0.03 to 0.5 μM plutonium solutions and about 0.1 to 4 μM neptunium solutions were used. Standard sorbate solutions (to which no sorbent was added and which were subjected to the same shaking treatment) were used to generate standard curves. No sorbate sorption onto the centrifuge tubes was detected.

Results and Discussion

Neptunium

Sorption as a function of tuff and oxide minerals.

The isotherms for neptunium sorption on different iron oxides are shown in Fig. 67. In this experiment, the three iron oxides were used as sorbents. Results show that, on a weight basis, hematite was the most adsorptive, whereas goethite was the least adsorptive. Thus, the sorption of neptunium on model iron oxides follows the order hematite > ferrihydrite > goethite.

Two things should be noted in this study. First, the surface areas of these iron oxides were different, and the sorptivity of neptunium was not compared on a unit surface-area basis. For ferrihydrite and goethite, the surface areas are around $90 \text{ m}^2/\text{g}$, whereas the surface area of hematite is about $40 \text{ m}^2/\text{g}$. Higher surface areas are expected to have higher sorptions. Secondly, the sorption experiments were not conducted at the same pH. Sorption on ferrihydrite was conducted at a pH of 6.2, whereas sorption on hematite and goethite were conducted at a pH of 6.9. The pH may affect the sorptivity of neptunium on iron oxides. The effect of pH on neptunium sorption will be presented in the next section.

The effect of oxide surface areas on neptunium sorption was replotted in Fig. 68. In this figure the amount of neptunium sorption was normalized on a unit surface-area basis (m^2). Results again showed that the sorption of neptunium on iron oxides follows the order hematite > ferrihydrite > goethite. Evidently, hematite has the highest sorptivity for neptunium on the basis of both weight and unit surface area.

Effect of pH on sorption.

To quantify organic sorption, it is required that we understand the effect of organics on radionuclide sorption. Experiments were conducted to study organic

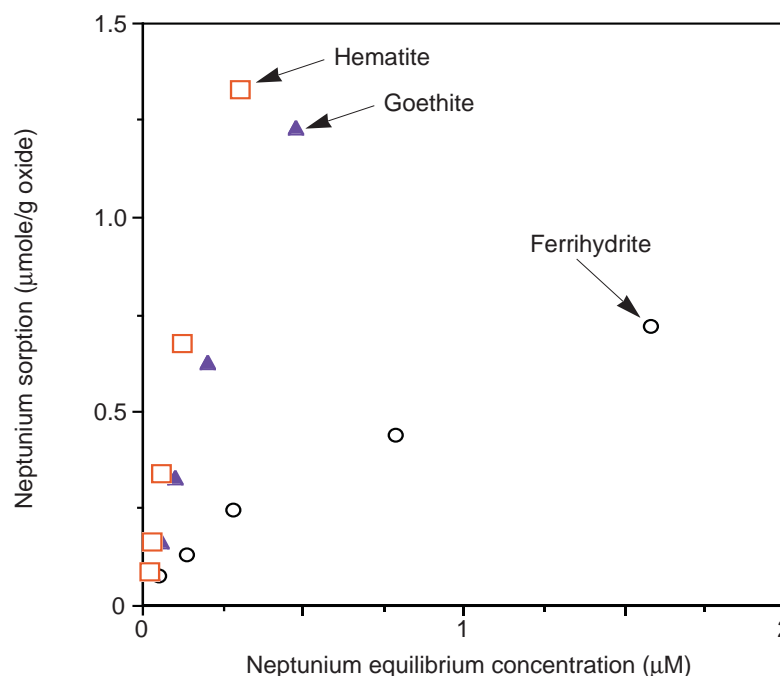


Figure 67. Neptunium Sorption per Unit Mass on Iron Oxides. The plot shows isotherms for the sorption of neptunium on three different iron oxides, calculated on the basis of unit mass.

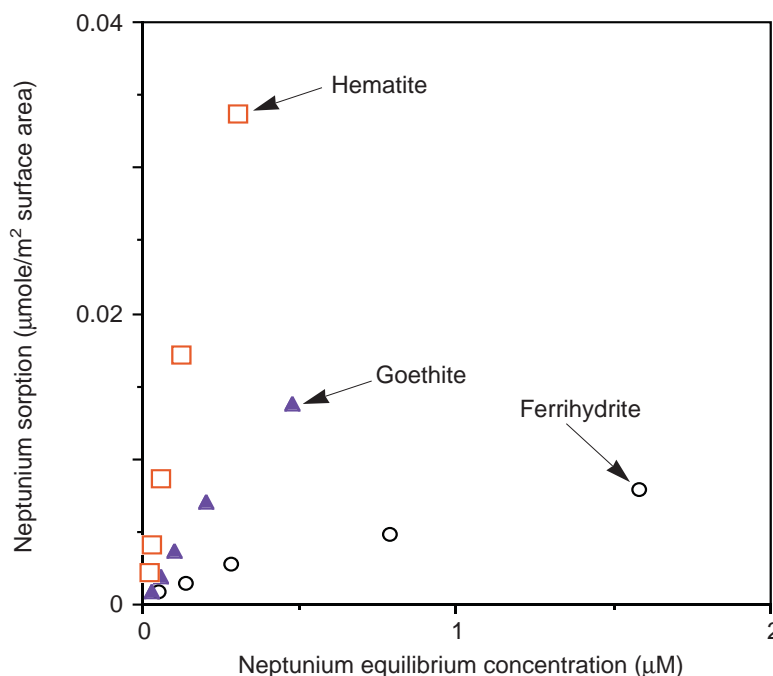


Figure 68. Neptunium Sorption per Unit Area on Iron Oxides. The plot shows isotherms for the sorption of neptunium on three different iron oxides, calculated on the basis of unit surface area.

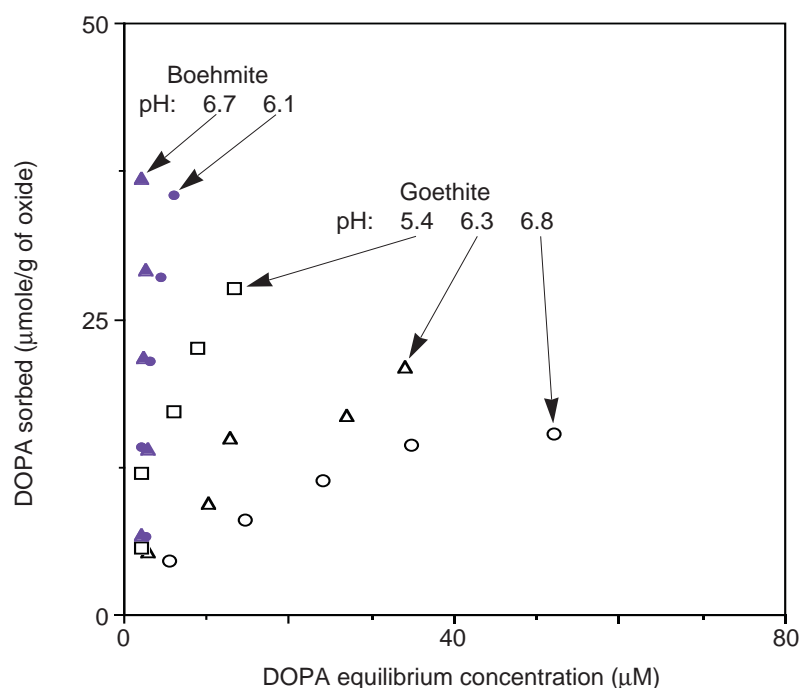


Figure 69. pH Dependence of DOPA Sorption on Oxides. This plot shows isotherms for the sorption of DOPA on goethite and on boehmite at different pH levels in the presence of 0.1 M KCl.

sorption, and the results are presented in this section. The isotherms for DOPA adsorption on goethite and boehmite at different pH levels are shown in Fig. 69. On a weight basis, boehmite was more adsorptive than goethite. The linear sorption curves for these oxides suggest a low degree of coverage of the surface reactive sites by the organic material in the presence of excess potassium chloride. This finding is consistent with the theoretical calculation of coverage, which suggests that the amount of DOPA sorption is much less than a monolayer, based on the BET surface area.

Increasing the solution pH resulted in a higher organic sorptivity for all oxides. Under neutral and slightly acidic conditions (pH values from 5.5 to 7), iron and aluminum oxides were expected to have positive surface charges (Sposito 1989). Although the sorption of DOPA is apparently not dependent on surface charge effects such as electrostatic attraction, it may be controlled by the deprotonation process of the organic material.

DOPA is expected to be dominated by neutral species under neutral and slightly acidic conditions, but raising the pH level will increase the concentration of deprotonated DOPA species, which are expected to have a stronger affinity for oxide surfaces in direct surface complexation. Therefore, it is reasonable to assume that DOPA forms direct surface bidentate complexes on the oxide surfaces.

The isotherms for neptunium sorption on goethite at different pH levels are shown in Fig. 70. Increasing the solution pH from 6.2 to 6.9 resulted in a higher neptunium sorptivity.

Effect of model organics on sorptive behavior.

We examined the effect of natural organics on radionuclide sorption onto natural tuff material that may have been precoated with natural organic material. The standard method for removing the natural organic material from mineral samples is to use hydrogen peroxide to oxidize the material (Kunze and Dixon 1986). We used a 15% hydrogen-peroxide solution when we removed organic material from crushed-tuff samples collected from Yucca Mountain. In the sorption experiments conducted to study the effect of the naturally presorbed organics on neptunium sorption, half of the tuff samples were treated with hydrogen peroxide, half were not.

Figure 71 shows the sorption isotherms of neptunium on both types of tuff samples. The results suggest that treatment with hydrogen peroxide had little or no effect on the sorption of neptunium onto the tuff material.

The lack of effect of hydrogen-peroxide treatment on neptunium sorption on tuff materials is attribut-

able to three factors. First, untreated tuff may contain very little or no organic material on its surface. Low organic content on the untreated tuff surface could be expected because crushed tuff material is generated from bedrock that may have little exposure to natural organic materials. New surfaces generated during the crushing process would not contain organic materials, in which case untreated tuff would be expected to behave essentially the same as tuff treated with hydrogen peroxide. Second, neptunium has intrinsically low sorptivity on tuff material. No observable difference in sorption on both treated and untreated tuff is attributed to the low sorption of neptunium on both sorbents. Any minute differences in sorption are likely to occur below the level of detection. Third, the sorption of neptunium may be unaffected by organic material, assuming that organic materials such as DOPA do not influence neptunium sorption on tuff, goethite, or boehmite.

To explore the possibility that the untreated tuff contained little organic material, 4 to 50 μM of DOPA was purposely added to both treated and untreated crushed tuff materials, and the sorption isotherms of neptunium on these systems were compared. As Figs. 72 and 73 illustrate, the addition of DOPA had no effect on neptunium sorption on either treated or untreated crushed-tuff materials. These data thus sup-

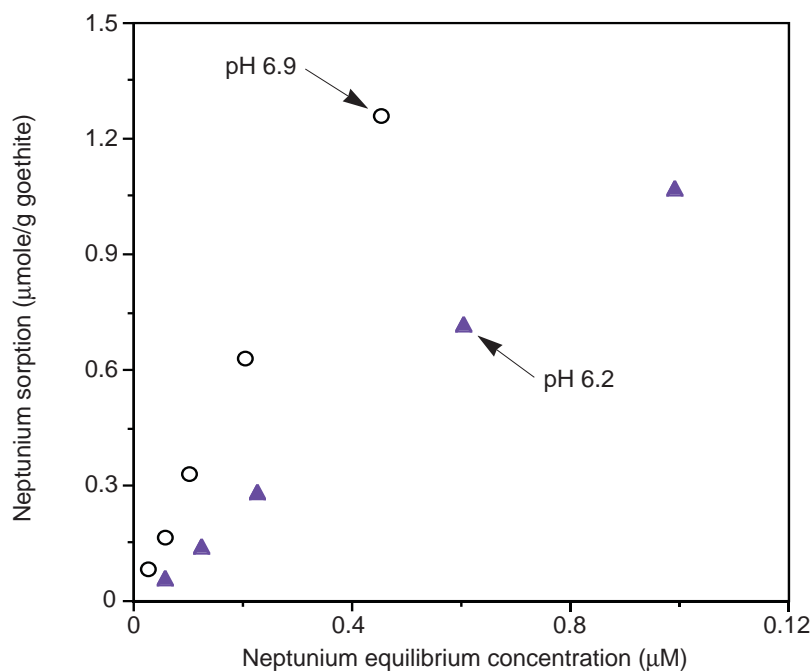


Figure 70. Neptunium Sorption on Goethite. This plot shows isotherms for the sorption of neptunium on goethite at a pH of 6.2 and 6.9.

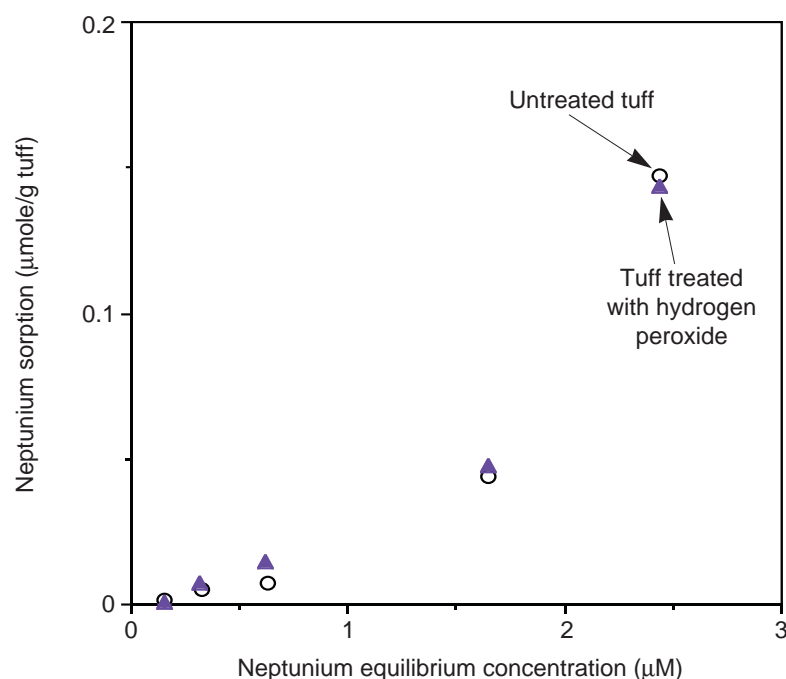


Figure 71. Neptunium Sorption on Treated and Untreated Tuff. This plot shows isotherms for the sorption of neptunium on devitrified tuff (G4-270) treated with hydrogen peroxide and untreated.

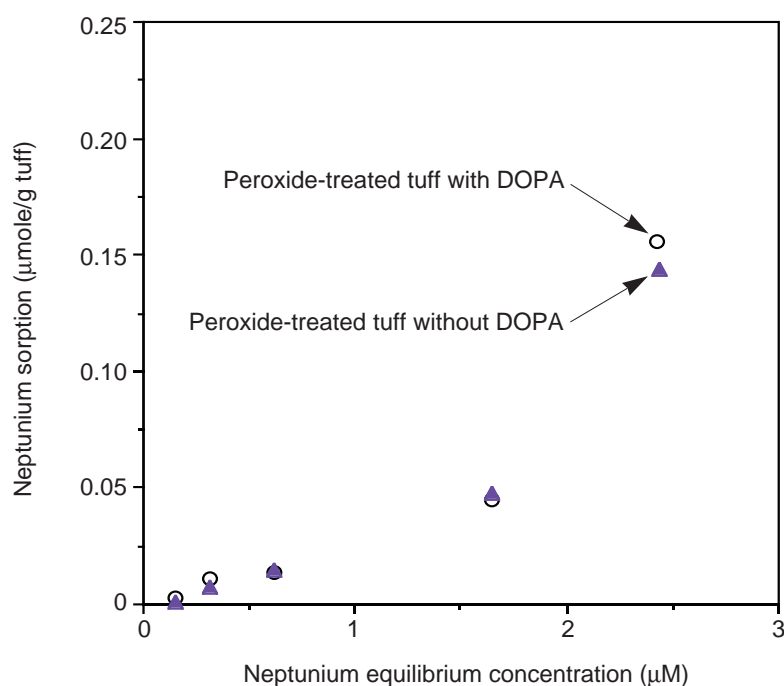


Figure 72. Sorption with and without DOPA on Treated Tuff.
This plot shows isotherms for the sorption of neptunium on hydrogen-peroxide-treated tuff materials (G4-270) with and without DOPA.

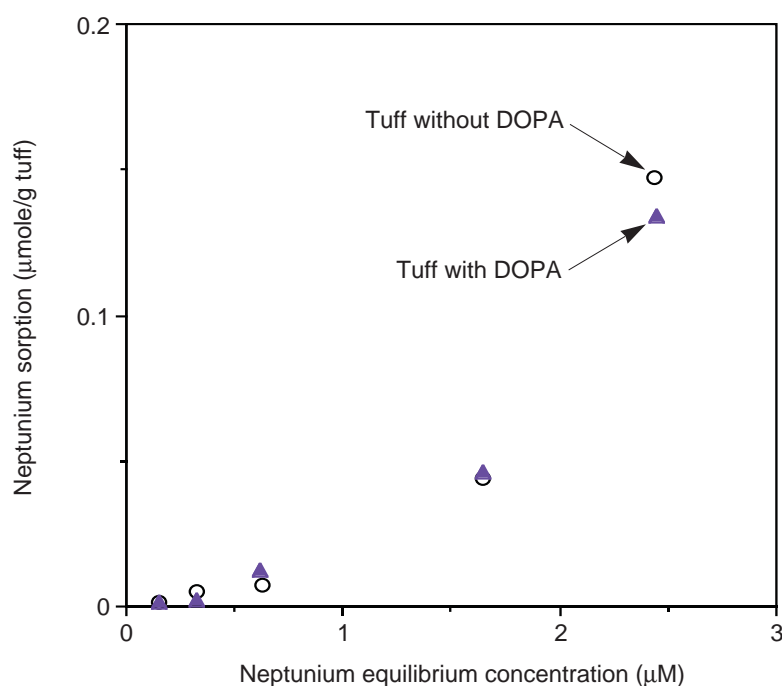


Figure 73. Sorption with and without DOPA on Untreated Tuff.
This plot shows isotherms for the sorption of neptunium on untreated tuff samples (G4-270) with and without DOPA.

port the premise that the presence of organic material does not affect neptunium sorption on tuff materials.

Because this experiment did not rule out the possibility that the lack of an observable effect was a result of the intrinsically low sorptivity of tuff materials, the sorption of neptunium on iron and aluminum oxides in the absence and presence of DOPA was examined. The sorption of neptunium is expected to be much higher on iron and aluminum oxides than on tuff material. Thus, any effect of DOPA on neptunium sorption ought to appear in the oxide systems. To verify this assumption, sorption isotherms were measured for neptunium on iron and aluminum oxides and tuff material in the absence of organic materials with 0.1 M KCl at a pH of 6.2. The results (Fig. 74) indicate that the sorptivity of boehmite and goethite is approximately one and two orders of magnitude higher, respectively, than the sorptivity of tuff material. Thus, any effect of DOPA on neptunium sorption should be easily detectable in these oxide systems.

Neptunium sorption isotherms on iron and aluminum oxides in the presence of DOPA are shown in Figs. 75 and 76. In these experiments, 0.1 M KCl was used to maintain an essentially constant ionic strength, and the final pH of the suspensions was adjusted to a value of 6.2. The

initial neptunium concentration ranged from 0.2 to 2 μM , and the initial DOPA concentration ranged from 4 to 50 μM . The sorption isotherms of neptunium on aluminum and iron oxides suggest that DOPA does not significantly affect the sorption of neptunium. The relatively weak complexation of the pentavalent neptunium ion is a result of its relatively low effective charge on the cation (Choppin and Rao 1984). These results imply that there is no significant influence of DOPA on neptunium sorption on aluminum and iron oxides.

The occurrence of surface complexation between DOPA and oxide surfaces is supported by the observed sorption of catechol on metal oxide, which indicates that catechol chemisorbs on metal oxide by forming a bidentate complex with the surface metal atoms. DOPA is an organic with functional groups like catechol (phenols) and alanine (amino acids). Thus, the effect of simple organics such as catechol and alanine on the sorption of neptunium was studied. Both catechol and alanine are expected to complex with metal ions in solution. Besides the formation of metal-organic complexes, catechol readily undergoes redox reactions with some metal and metal oxides (McBride and Wesselink 1988). For example, catechol at high concentrations may undergo electron-transfer reactions with manganese and iron oxides.

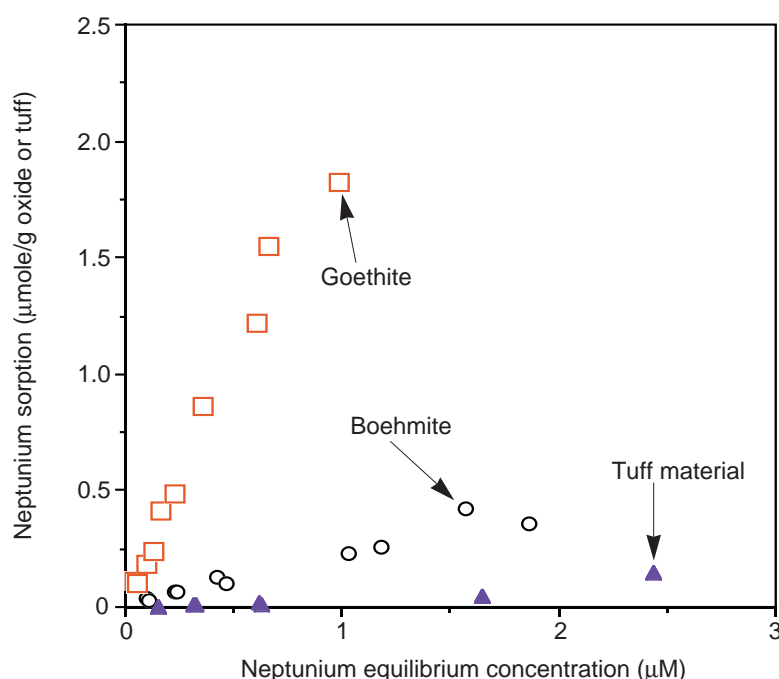


Figure 74. Neptunium Sorption on Oxides and Tuff. This plot shows isotherms for the sorption of neptunium on goethite, boehmite, and tuff material (G4-270).

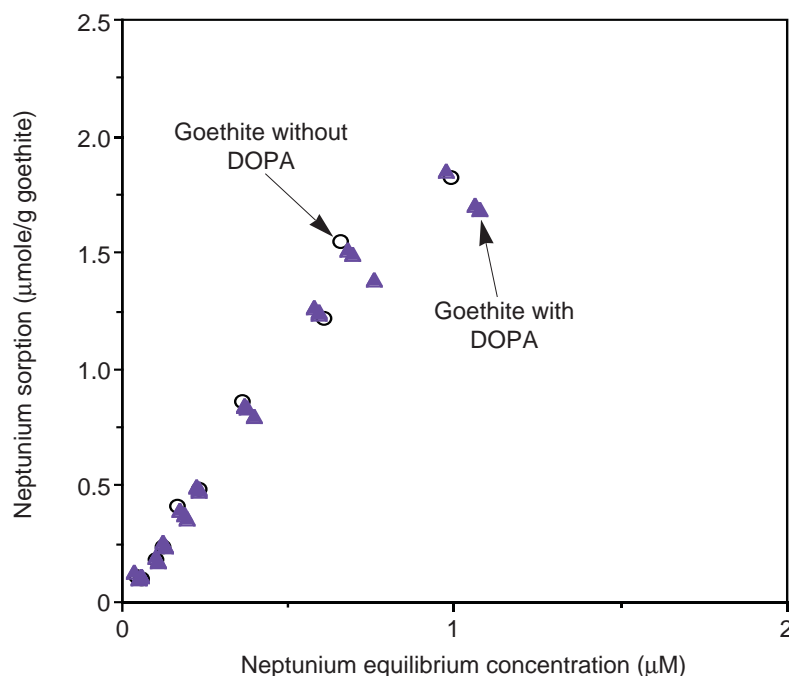


Figure 75. Sorption on Goethite with or without DOPA. This plot shows isotherms for the sorption of neptunium on goethite in the presence and absence of DOPA at a pH of 6.2.

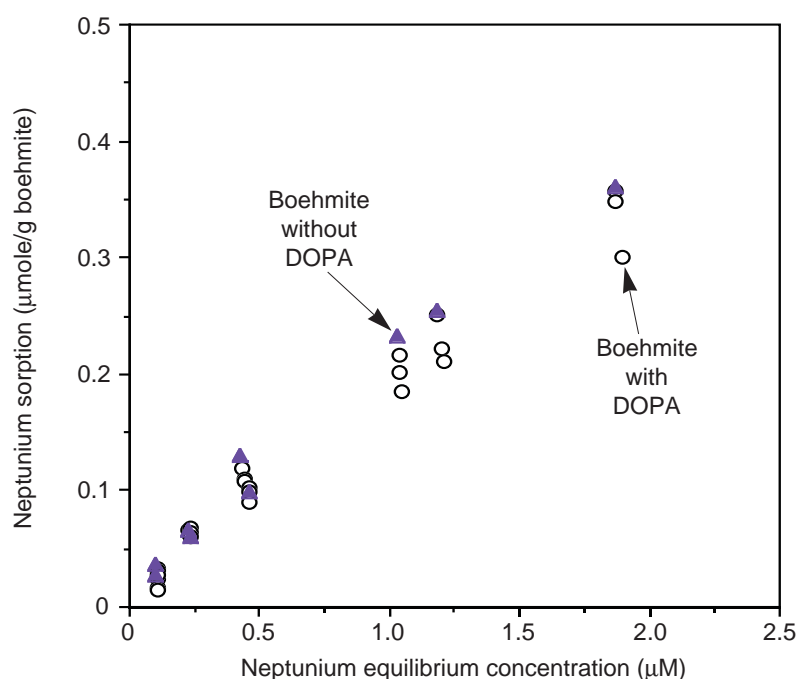


Figure 76. Sorption on Boehmite with or without DOPA. This plot shows isotherms for the sorption of neptunium on boehmite in the presence and absence of DOPA at a pH of 6.2.

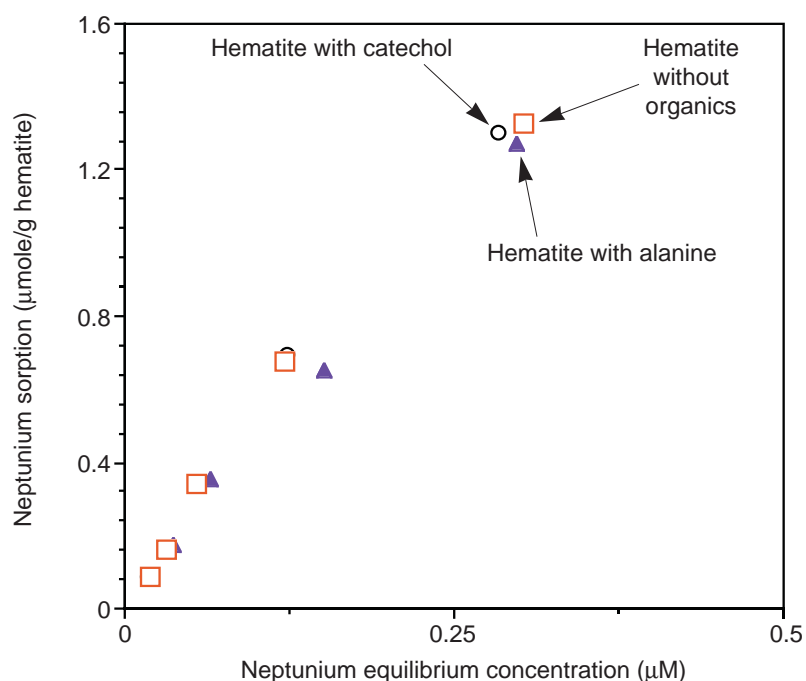


Figure 77. Sorption on Hematite with or without Organics. This plot shows isotherms for neptunium sorption on hematite in the presence and absence of catechol or alanine (1 μM) at a pH of 6.9.

We quantified the effect of catechol and alanine on neptunium sorption by measuring isotherms for sorption on hematite, ferrihydrite, and goethite in the presence and absence of catechol and alanine (Figs. 77 to 79). In these experiments, 0.1 M KCl was used to maintain an essentially constant ionic strength. The final pH of the suspensions was adjusted to 6.2 for ferrihydrite and to 6.9 for goethite and hematite. The initial neptunium concentration ranged from 0.2 to 2 μM, and the initial catechol and alanine concentrations were 1 μM. The sorption isotherms of neptunium on iron oxides suggest that catechol and alanine does not significantly affect the sorption of neptunium. The implication of these results is that there is no significant influence of catechol and alanine on neptunium sorption on different iron oxides.

Although both catechol and alanine may complex with neptunium in solution, the organic-metal complexes are apparently not strong enough to affect the neptunium sorption. These results are consistent with the data of Fig. 75 for the iron oxide, goethite, which indicate that DOPA has no effect on neptunium sorption.

In another set of experiments to study the effect of naturally occurring organic material on neptunium sorption, NAFA served as the model fulvic material. The isotherms for the sorp-

tion of neptunium on boehmite in the presence and the absence of NAFA are shown in Fig. 80 and for the sorption of neptunium on goethite in Fig. 81. Similar isotherms for the sorption of neptunium on treated tuff materials are shown in Fig. 82 and for untreated tuff materials in Fig. 83. In these experiments, 0.1 M KCl was used as the background electrolyte, and the final pH was adjusted to 6.2. Initial neptunium concentrations ranged from 0.2 to 3 μM , and the NAFA concentrations ranged from 0.1 to 0.4 ppm.

As shown in Figs. 80 to 83, the fulvic material NAFA had little effect on neptunium sorption in all systems. Thus, we concluded that organics do not affect the sorption of neptunium both in simple, low-molecular-weight organics and in naturally occurring fulvic organic material. The lack of detectable effects of organics on neptunium sorption is possibly attributable to the stable redox state of Np(V) in solution and to low complexation between neptunium ions and organic chemicals.

Plutonium

Sorption as a function of tuff and oxide minerals.

Plutonium sorption on different iron oxides is shown in Fig. 84. On a weight basis, hematite was the most adsorptive, whereas goethite was the least adsorptive. The sorption of plutonium on model iron oxides follows the order hematite > ferrihydrite >

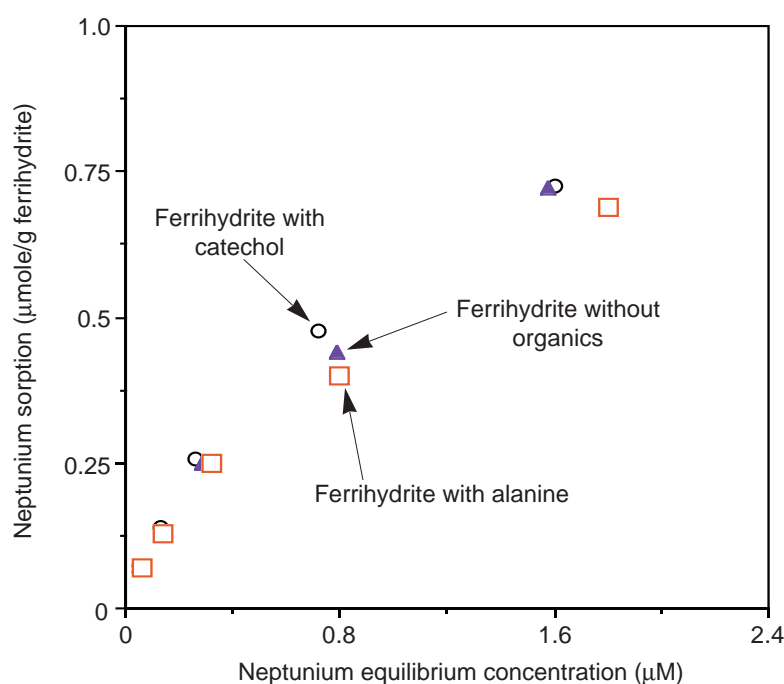


Figure 78. Sorption on Ferrihydrite with or without Organics.

The plot shows isotherms for sorption of neptunium on ferrihydrite in the presence and absence of catechol or alanine (1 μM) at pH 6.2.

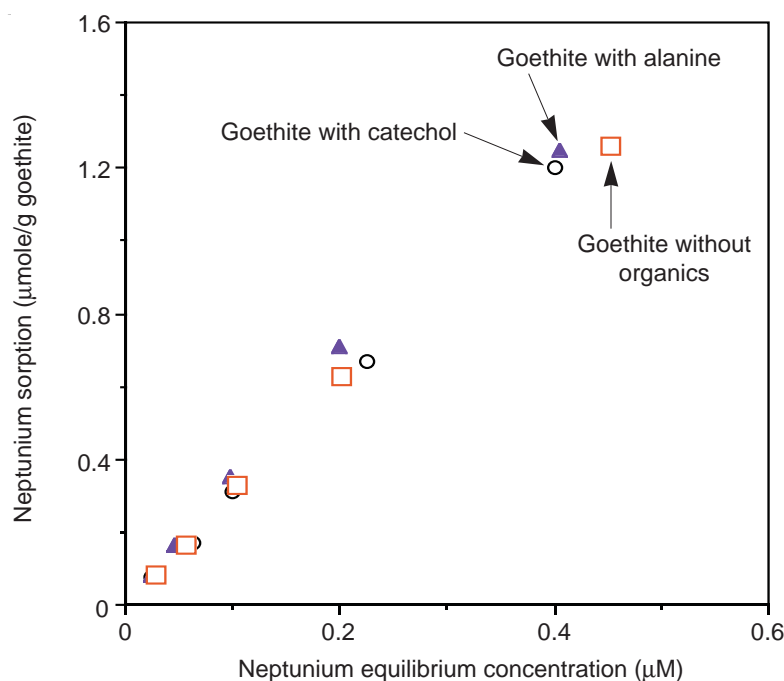


Figure 79. Sorption on Goethite with or without Organics. This plot shows isotherms for the sorption of neptunium on goethite in the presence and absence of catechol or alanine (1 μM) at a pH of 6.9.

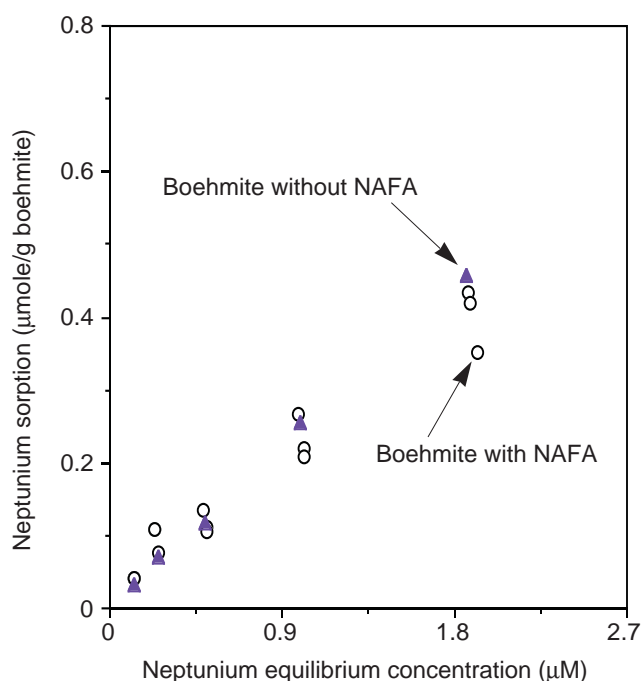


Figure 80. Boehmite with or without NAFA. This plot shows isotherms for the sorption of neptunium on boehmite with and without NAFA.

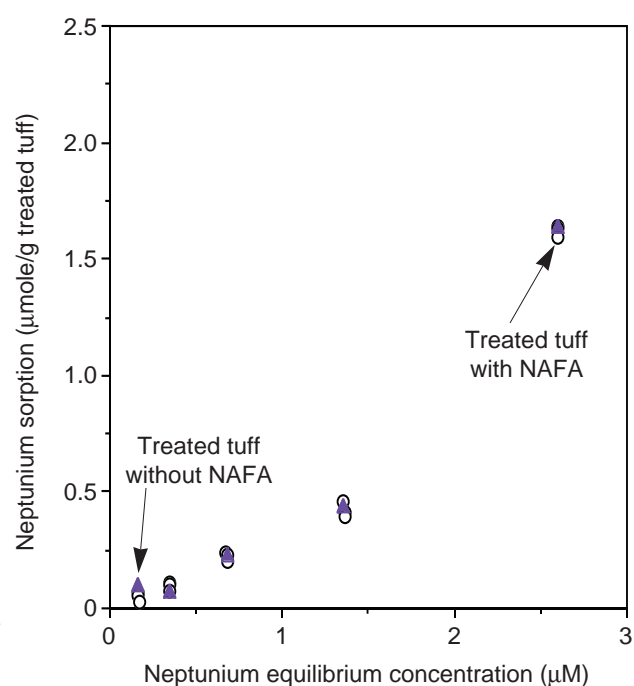


Figure 82. Treated tuff with or without NAFA. This plot shows isotherms for neptunium sorption on treated tuff (G4-270) with and without NAFA.

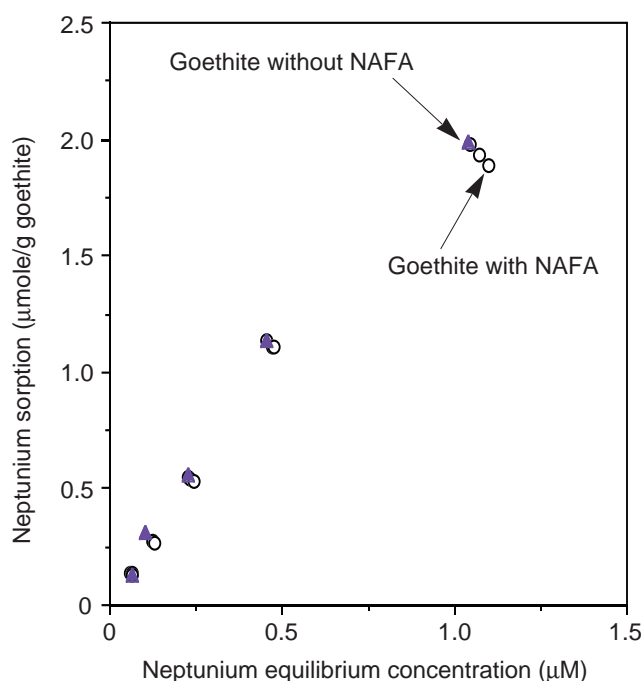


Figure 81. Goethite with or without NAFA. This plot shows isotherms for the sorption of neptunium on goethite with and without NAFA.

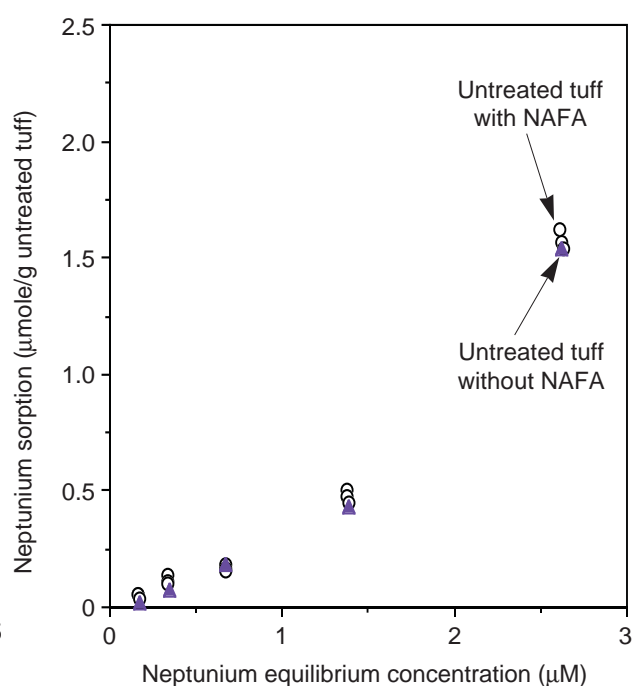


Figure 83. Untreated tuff with or without NAFA. This plot shows isotherms of neptunium sorption on untreated tuff (G4-270) with and without NAFA.

goethite. Thus, for both neptunium and plutonium, hematite is the most adsorptive, but goethite and ferrihydrite reverse order.

As was the case for neptunium, two things should be noted in this result for plutonium. First, the surface area of these iron oxides were not the same. For ferrihydrite and goethite, the surface areas are around $90 \text{ m}^2/\text{g}$; for hematite, the surface area is about $40 \text{ m}^2/\text{g}$. Second, the sorption experiments were not conducted at the same pH. The sorption on ferrihydrite was conducted at a pH of 6.1; the sorptions on hematite and goethite were conducted at a pH of 6.9.

The effect of oxide surface areas on plutonium sorption was replotted in Fig. 85, with the amount of plutonium sorption normalized to unit surface area (m^2). Results again showed that the sorption of neptunium on model iron oxides follows the order hematite > ferrihydrite > goethite.

Effect of pH on sorption.

The isotherms for plutonium sorption on goethite at two different pH levels are shown in Fig. 86. Increasing the solution pH from 6.6 to 6.9 resulted in a higher plutonium sorptivity. It should be noted that the initial plutonium concentration was the same for both isotherms; however, the amount of goethite was different. The linear sorption curves suggest a low degree of coverage of the surface reactive

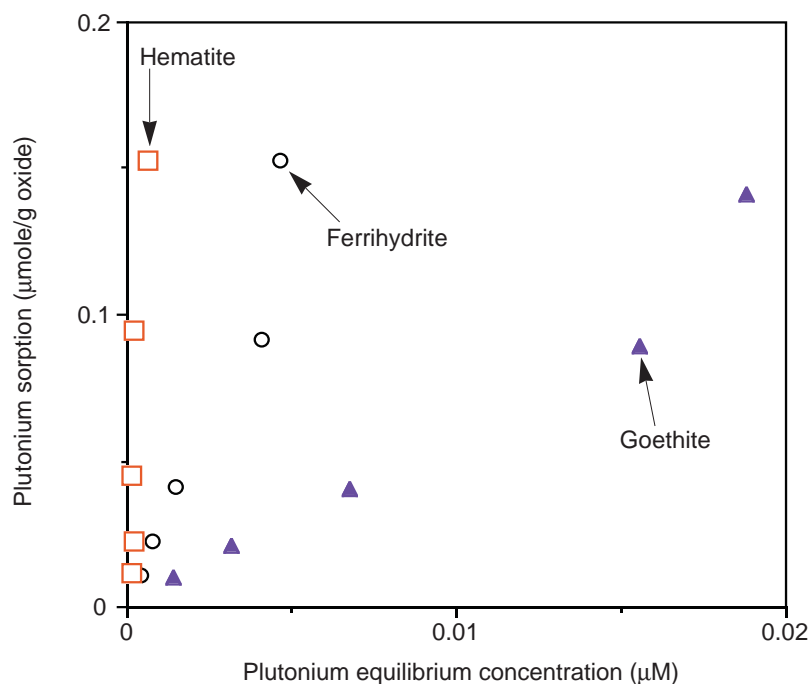


Figure 84. Plutonium Sorption per Unit Mass on Iron Oxides.

This plot shows isotherms for the sorption of plutonium on three iron oxides, calculated on the basis of unit mass.

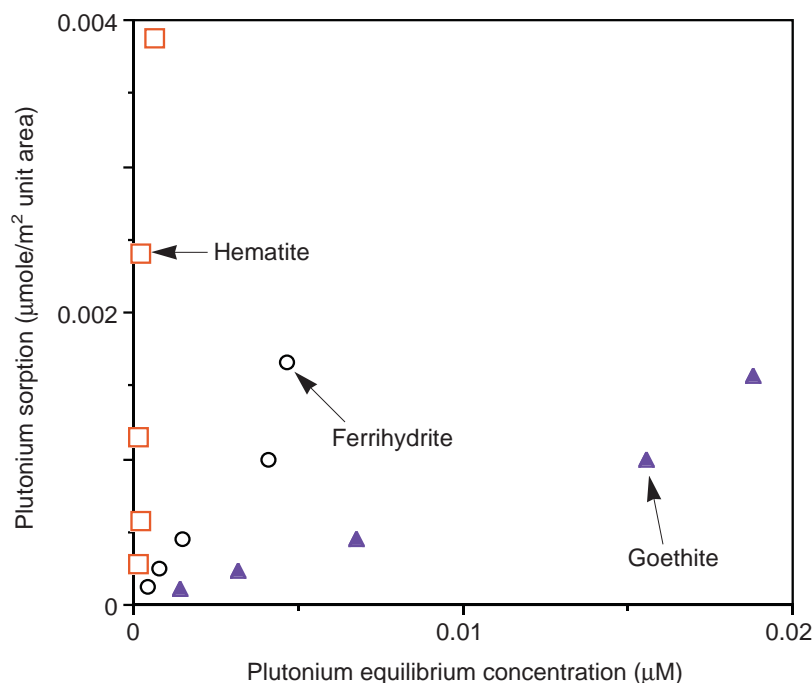


Figure 85. Plutonium Sorption per Unit Area on Iron Oxides.

This plot shows isotherms for the sorption of plutonium on three different iron oxides, calculated on the basis of unit surface area.

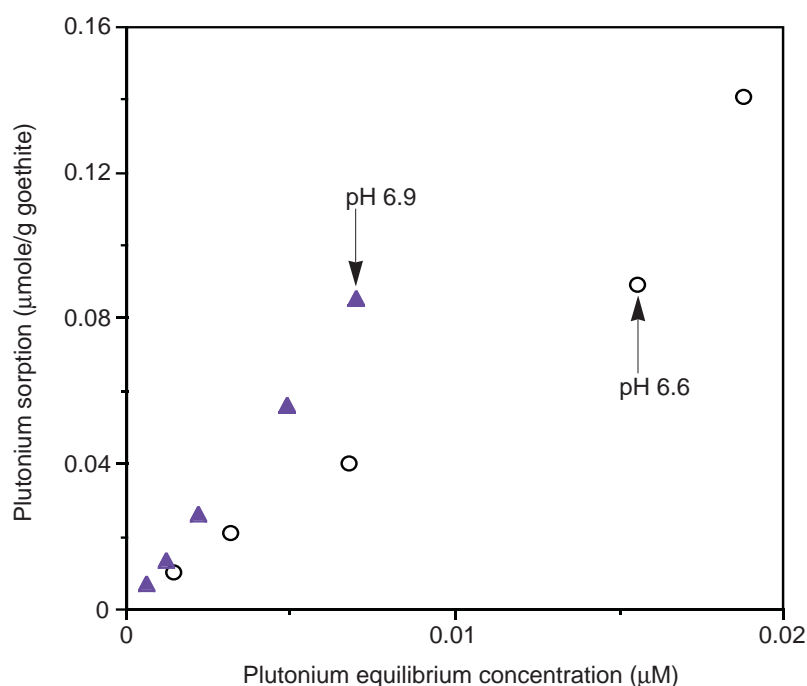


Figure 86. pH Dependence of Plutonium Sorption on Goethite.

This plot shows isotherms for the sorption of plutonium on goethite at two different values of pH.

shown in Fig. 87, and the isotherms for plutonium sorption on goethite and hematite in the presence of catechol and alanine are shown in Fig. 88. The isotherms clearly demonstrate that the sorption of plutonium onto goethite and ferrihydrite was affected by the presence of the organic materials.

The amount of plutonium sorption on goethite and ferrihydrite was lower in systems that contained alanine than in systems that contained no alanine.

Apparently, the presence of alanine suppressed the plutonium sorption on the surface of these iron oxides, probably because of a lowering of the free plutonium-ion activity in solution by the formation of an alanine-plutonium complex.

sites by plutonium ions in the presence of excess potassium chloride. This finding is consistent with the theoretical calculation of coverage, which suggests, based on BET surface areas, that the amount of plutonium sorption is much less than a monolayer.

Increasing the solution pH resulted in a higher plutonium sorptivity. Under neutral conditions (a pH of 7), goethite is expected to have positive surface charges. However, the sorption of plutonium on goethite was found to increase as solution pH increased. The sorption of plutonium is apparently not dependent on ion exchange because iron oxide should have no cation-exchange capacity. The sorption is believed to be controlled by a surface-complexation process because plutonium is expected to be dominated by the cationic species PuO_2^+ under neutral and slightly acidic conditions.

Effect of model organics on sorptive behavior.

The isotherms for plutonium sorption on ferrihydrite in the presence of catechol and alanine are

Conversely, the amount of plutonium sorption on goethite and ferrihydrite was higher in the presence of catechol than it was in the absence of catechol. Evidently, catechol enhanced the sorption.

However, the effect of catechol and alanine on plutonium sorption was not found in the hematite system. The presence of these organic materials had little effect on the sorption of plutonium on hematite (Fig. 88). The lack of an observable effect in this case is probably a result of the intrinsically high sorptivity of plutonium on hematite. Any small enhancement or suppression of sorption that might be attributed to catechol and alanine under such a high sorptivity would not be detected.

Overall, the results of our study suggest that the model organic materials catechol and alanine do affect the sorption of plutonium on iron oxides.

The isotherms for sorption of plutonium on ferrihy-

drite and goethite in the absence of DOPA and in its presence at three concentration levels (1, 0.1, and 0.01 μM) clearly demonstrate (Figs. 89 and 90) that such sorption was affected by the presence of the organic material DOPA. Plutonium sorption was higher in systems that contained DOPA than in systems that contained no DOPA. Furthermore, sorptivity increased as the initial DOPA concentration increased from 0.01 to 1 μM . Evidently, the presence of DOPA enhanced the sorption of plutonium on goethite and ferrihydrite. This result is likely attributable to the formation of stable surface DOPA-plutonium ternary complexes and to a redox reaction between DOPA and plutonium. Reduction of Pu(V) to lower oxidation states will enhance the sorption/precipitation of the plutonium.

For neptunium, however, the effect of DOPA on sorption was not found in goethite (Fig. 75), boehmite (Fig. 76), and tuff material (Fig. 73). The presence of DOPA had little effect. It is possible that DOPA does not complex with neptunium in solution or that DOPA cannot reduce Np(V) to lower oxidation states. Such relatively weak complexation is possibly a result of the relatively low effective charge on the cation (Choppin and Rao 1984), consistent with the fact that neptunium complexed weakly with a natural humic material extracted from a groundwater (Kim and Sekine 1991).

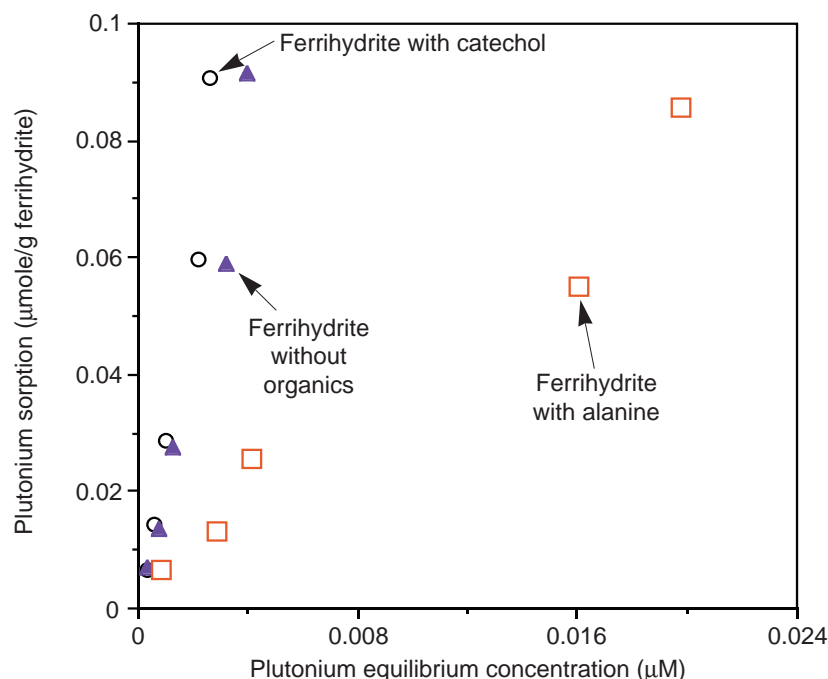


Figure 87. Sorption on Ferrihydrite with and without Organics.

This plot shows isotherms for plutonium sorption on ferrihydrite with and without catechol or alanine (1 μM) at a pH of 6.2 in 0.1 M KCl.

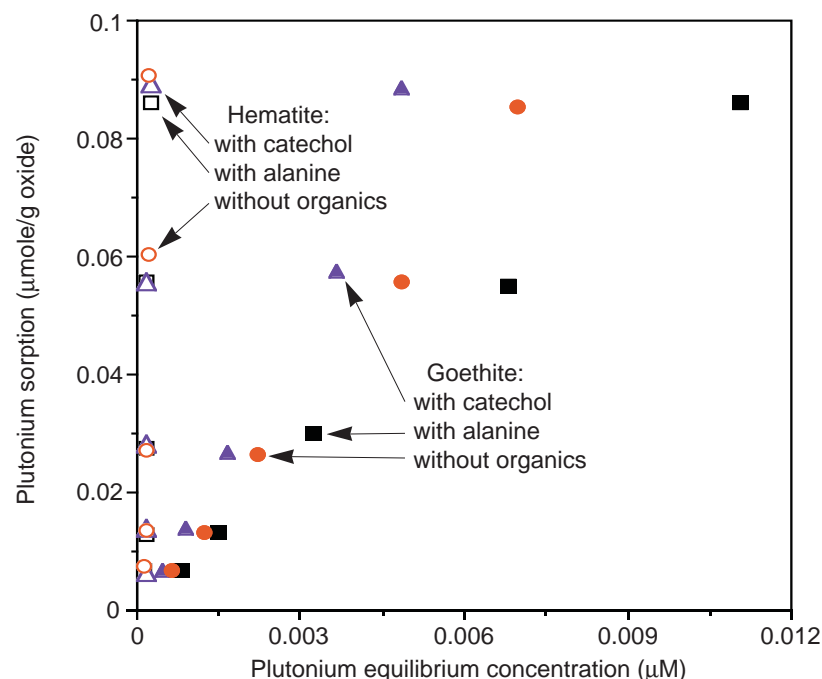


Figure 88. Sorption with and without Organics. This plot shows isotherms for the sorption of plutonium on hematite and goethite with and without catechol or alanine at a pH of 6.9 in 0.1 M KCl.

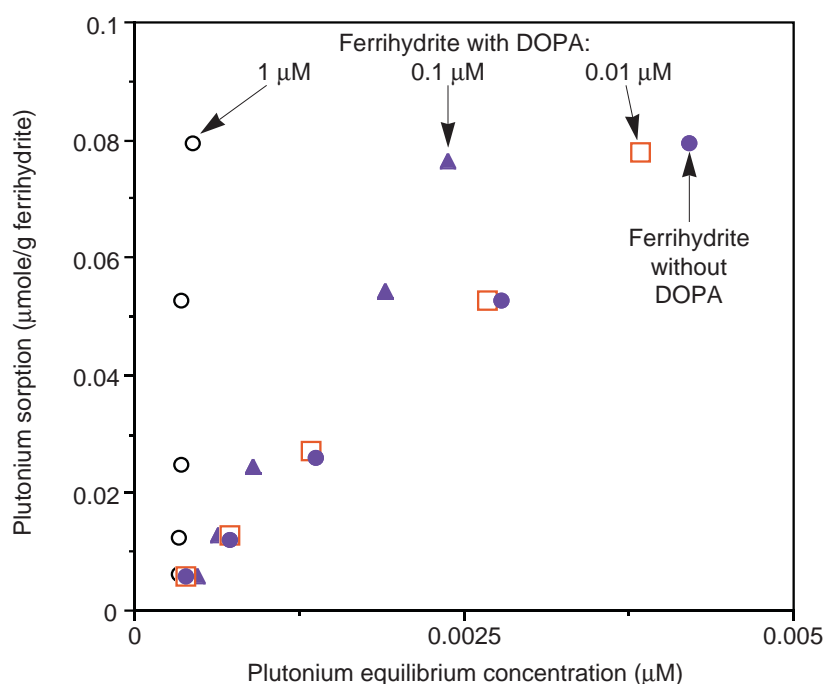


Figure 89. Sorption on Ferrihydrite with and without DOPA.

This plot shows isotherms for the sorption of plutonium on ferrihydrite with and without DOPA at a pH of 6.2 in 0.1 M KCl.

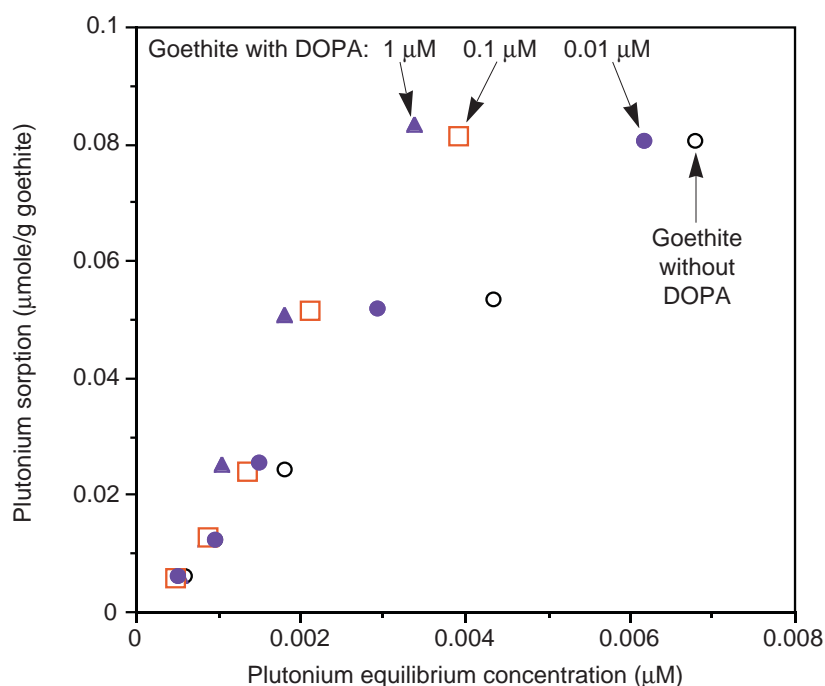


Figure 90. Sorption on Goethite with and without DOPA. This plot shows isotherms for the sorption of plutonium on goethite with and without DOPA at a pH of 6.9 in 0.1 M KCl.

Summary

From the sorption data, the following conclusions can be drawn concerning the effect of natural organic materials on the sorption of neptunium and plutonium by iron and aluminum oxides and by crushed-tuff material:

- The sorption of model organic material DOPA on oxide surfaces follows the order aluminum oxide > iron oxide. For a given sorbent, the higher the pH, the more DOPA is sorbed. Surface complexation is the most likely sorption mechanism.
- The sorption of plutonium on iron oxides generally follows the order hematite > ferrihydrite > goethite. The sorption of neptunium on iron oxide is higher than that on aluminum oxide. The sorption of neptunium on crushed-tuff material was much lower than that on oxide surfaces.
- The sorption of plutonium and neptunium on iron oxides increases as the solution pH is raised. The sorption of plutonium on hematite, goethite, and ferrihydrite is much higher than that of neptunium.
- The amount of neptunium sorption was not affected by any of the organic materials that were studied. The presence of the model organic materials of alanine, catechol,

DOPA, and NAFA did not influence the sorption of neptunium on tuff or on iron and aluminum oxides. This lack of an observable effect is presumably a result of the weak complexation between neptunium and the model organics.

- The sorption of plutonium was influenced by the presence of DOPA on goethite and ferrihydrite. Increasing the amount of DOPA resulted in higher sorption of plutonium on goethite and ferrihydrite. Alanine decreases the sorption of plutonium. However, in the system containing catechol, plutonium sorption was increased. The enhancement of plutonium sorption in the presence of catechol is probably due to the reduction of Pu(V) to Pu(IV) by the organic. The inhibition of plutonium sorption in the presence of alanine is probably caused by the lowering of the free plutonium-ion activity in solution by formation of an alanine-plutonium complex. No observable effect of organics on plutonium sorption was found in the hematite system, which is probably due to a relatively high sorptivity of plutonium on the hematite surface.